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HYDROTHERMAL INTERACTION OF TOPOPAH SPRING TUFF WITH J-13 WATER AS A FUNCTION OF TEMPERATURE

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ABSTRACT

In support of the Nevada Nuclear Waste Storage Investigations Project experiments were conducted to study the hydrothermal interaction of rock and water representative of a potential repository in tuff. These experiments provided data relevant to near-field repository conditions that can be used to: assess the ability to use "accelerated" tests based on the SA/V (surface area/volume) parameter and temperature; allow the measurement of chemical changes in phases present in the tuff before reaction as well as the identification and chemical analysis of secondary phases resulting from hydrothermal reactions; and demonstrate the usefulness of geochemical modeling in a repository environment using the EQ3/6 thermodynamic/kinetic geochemical modeling code. Crushed tuff and polished wafers of tuff were reacted with a natural ground water in Uickson-type gold-cell rocking autoclaves which were periodically sampled under insitu conditions. Results were compared with predictions based on the EQ3/6 geochemical modeling code. Eight short-term experiments (2 to 3 months) at 150°C and 250°C have been completed using tuff from both drillcore and outcrop. Long-term experiments at 90°C and 150°C using drillcore polished wafers are in progress. This paper will focus on the results of the 150°C and 250°C experiments using drillcore polished wafers.

INTRODUCTION

Under anticipated conditions the initial response of the near-field environment to the heat generated by the emplacement of nuclear waste packages is an increase in temperature sufficient to dry out the partially-saturated host rock. Following the thermal pulse the rock cools and liquid water re-enters the near-field. As the water passes through the heated rock its composition is altered by interaction at temperatures of ~100°C. This altered water interacts with the waste packages by corroding canisters and dissolving the waste form. To estimate the magnitude of these reactions, the water composition must be known. Repository scale thermal modeling suggests potential for the existence of liquid water in pores at up to 140°C in cases with no venting [1], and package scale modeling shows waste centerline temperatures up to 230°C [2]. These estimates place upper bounds on experimental conditions appropriate for unanticipated but possible scenarios. Testing at these temperatures also aids in developing geochemical modeling computer codes by accelerating rates of reaction. This paper presents the results of such tests and compares the results to those predicted by the EQ3/6 geochemical modeling code [3].

MATERIALS AND METHODS

The rock wafers were cut from drillcore samples taken from potential repository depth in hole USW G-1 at Yucca Mtn. The rock is a densely welded, devitrified, vapor-phase altered, crystal-poor, rhyolitic ashflow tuff, the Topopah Spring Member of the Paintbrush Tuff [4]. The wafers were 1.0 in. dia. X 0.1 in. thick, hand-polished and ultrasonically cleaned in distilled water. The water was taken from well J-13 in Jackass Flat east of Yucca Mtn which produces largely from the Topopah Spring Member. This ground water is being used by the NNWSI Program as representative of water from the unsaturated zone and is well-characterized [5].

Experiments were run at 150°C and 250°C for 66 days using Dickson-type gold-cell rocking autoclaves [6] modified to hold rock wafers. Fluid samples were taken periodically for pH, cation (ICP-ES) and anion (IC) analyses. The Ar BET gas adsorption surface areas measured on the rock wafers indicate typical experimental SA/V ratios of 40 cm⁻¹. At the termination of each run the rock wafers were removed as rapidly as possible and rinsed thoroughly in distilled water, dried and C-coated for SEM observation and EMP analysis using both EDS and WDS.

DISCUSSION OF ANALYTICAL RESULTS

The fluid analyses are plotted versus time in Figures 1 and 2 for the 150°C and 250°C experiments, respectively.

In the 150°C experiment the Al concentration increased rapidly at first from the initial J-13 value (0.03ppm) to a maximum of 1.2ppm but then decreased to a concentration of 0.5ppm, which suggested kinetically inhibited precipitation. The Si concentration increased exponentially from the J-13 value (29ppm) to a value close to cristobalite saturation (122ppm) by the end of the run. The Ca concentration decreased quickly from 12ppm to 6ppm and Mg initially at 1.9ppm was removed to low levels (<0.1ppm). K resembled Al and after an initial rise from 4.6ppm to 6.5ppm decreased to 4.9ppm. Na showed a somewhat irregular slow rise from approximately 41ppm to 45ppm. The quenched pH dropped to a value of 6.8 and remained constant. Other than a decrease in CO₂ there was no significant change in anion content. The more complex behavior of Ca, K, and Al reflect the effects of dissolution of reactants and precipitation of metastable run products.

The effects of hydrothermal alteration of the host rock phenocrysts at 150°C were seen as highlighting of twinning by the formation of etch pits on feldspars, and the general corrosion of biotite. The smaller alkali feldspar crystals formed by granophyric devitrification of the host rock matrix and from vapor-phase deposition in lithophysal cavities appeared to be particularly prone to hydrothermal attack as did the other fine-grained devitrification products making up the matrix. Quantitative WDS analyses showed no compositional changes in the phenocrysts or matrix phases of the host rock as a result of hydrothermal alteration.

SEM observation of the surface of the core wafer was used to study secondary minerals formed at 150°C (Figure 3). Based on chemical composition determined by EDS analyses and on SEM morphology these are thought to include: illite, Mg-, Ca- &/or Fe-rich clays, gibbsite, calcite and a pure Si phase (cristobalite?). The "clays" (illite/montmorillonite) were dominant and the other phases much less abundant. The total amount of reaction products was quite small.

The solution analyses in the 66-day 250°C experiment (Figure 2) showed that Al increased rapidly at first to 3.6ppm, then decreased exponentially to a minimum of 1.6ppm, and finally began to rise again towards the end of the experiment reaching 3ppm. Si increased exponentially to cristobalite saturation (350ppm) taking 2 wks to reach steady-state. Ca was removed quickly to low levels (<1ppm) and Mg was completely removed (<0.1ppm). The K generally followed the Al trend as at 150°C, except that after initially rising to 6.5ppm it fell in an erratic manner and reached concentrations approximately equal to the starting value. Na showed a slight decline from the starting concentration. The quenched pH dropped to about 6.3 and remained constant. The CO₂ decreased while F and Cl increased slightly and other anions remained constant. Al, K and Ca again displayed the most complex behavior.

Hydrothermal alteration of the tuff at 250°C resulted in a secondary mineral assemblage that was different from that formed at 150°C (Figure 4). The dominant secondary mineral produced was the zeolite dachiardite. Abundant large prismatic crystals with smaller interpenetrant crystals and rosettes of crystals were produced. A cluster of crystals hand-picked from the surface of the wafer was run in a Gandolfi X-ray camera to make a positive identification and to measure d-spacings for calculation of cell constants using a linear regression technique. A polished grain mount of dachiardite crystals was analyzed by WDS and these results as well as the characterization described above have been reported elsewhere [7]. In the 250°C experiment other secondary minerals observed were: mordenite, clay (illite/montmorillonite), and a pure Si phase (cristobalite?). Dachiardite and mordenite were far more abundant than the other phases. The total amount of reaction products was much greater at 250°C than at 150°C.

GEOCHEMICAL MODELING OF 150°C EXPERIMENT

The rock/water interactions observed between the Topopah Spring Tuff and J-13 groundwater at 150°C in a closed system were simulated using the EQ3/b reaction path code. Water from well J-13 analyzed at day 0 was used as the initial solution composition. EQ3NR was used to generate the model aqueous solution. The dissolved aluminum concentration in the model solution was constrained to satisfy the mineral solubility equilibria for kaolinite in order to initially reduce the number of supersaturated mineral phases in the solution. The Topopah Spring Tuff was represented by an assemblage of six minerals; alkali feldspar, plagioclase, cristobalite, quartz, biotite, and montmorillonite based on the petrologic description given by Warren et al. [8]. The surface area of the core wafer (determined by BET Ar method) and the volume percent of

each phase were used to estimate the specific surface area for the individual minerals. Dissolution rate constants for quartz and cristobalite were calculated at 150°C using the data given by Rimstidt and Barnes [9]. The rate constants used for the feldspars and biotite were based on estimates that assume dissolution of the solid is controlled by surface reactions ($E_{act} = 14$ kcal for grain size $\sim 100\mu$ [10]). The estimated values were then reduced by approximately an order of magnitude to account for the smaller surface area of the wafer and decreased surface reactivity caused by ultrasonic cleaning. A relative rate constant was used for montmorillonite that assumed dissolution of the phase was complete within 5 days. The code was constrained to suppress all silica minerals less soluble than cristobalite. An additional phase, maximum microcline was eliminated from phases allowed to precipitate because the primary feldspar is represented by sanidine.

The EQ3/6 calculations realistically predict that none of the initial reactants are exhausted and a relatively minor amount of the rock dissolves during the given run interval. The final concentrations of all major cations in solution predicted by the model closely approach the final measured cation compositions for these elements (Figure 1). As silica (primarily cristobalite and quartz) dissolves, its concentration is shown to increase to a steady-state value that approaches cristobalite solubility near the latter stages of the experiment. Na, Al, and Mg show fairly constant trends over the run interval. The sharp rise in Al concentration can be attributed to rapid dissolution at 150°C of the small amount of montmorillonite present in the host rock. The initial drop in Ca concentration is due to the formation of minor calcite. The continued gradual decrease in Ca throughout the experiment is due to the precipitation of Ca-smectite. The formation of smectite also coincides with a drop in Al concentration in the same interval. The sharp rise in the K concentration during the first few days of the experiment cannot be accounted for by the dissolution of the major potassium phase, sanidine. The only other phase present containing significant K in the host rock is biotite. The kinetic rate laws available in the current version of EQ6 provide only for dissolution reactions. Precipitation appears in EQ6 only as an instantaneous process once saturation is reached, although the incorporation of precipitation rate laws is currently in progress. These results can be used to estimate the rate of precipitation of secondary phases observed in the altered wafers. It is probably reasonable to assume that the secondary phase represented by the K-sink will have to be represented theoretically by a metastable illite or smectite, because metastable phases typically precipitate quickly from solution, often with variable cation compositions that change as the composition of the solution changes. Although these preliminary modeling results can not account for all secondary phases determined by SEM observation and EDS analysis, these results indicate the importance of the careful characterization of secondary mineral assemblages, and the great need for theoretical representation of metastable phases when modeling low temperature natural systems. Data for the 250°C experiment have not been modeled because no thermodynamic data exists for the dominant mineral (dachardite) observed in the alteration assemblage.

CONCLUSIONS

These experiments investigate the pore water chemistry in tuff as it is modified by a heat source such as a HLW repository. The altered water chemistry differs primarily in dissolved silica, which is determined by cristobalite solubility. The water remains relatively benign with respect to waste package survivability, especially with regard to its anion content and pH [11]. The dominant secondary minerals produced (clays and zeolites) have high surface areas, high CEC and positive sorption capabilities and thus may help to reduce radionuclide mobility in the near-field. In the far-field silica may precipitate as the altered water moves down the thermal gradient away from the heat source. These experiments showed that increased temperature yields a different metastable mineral assemblage and probably can not be used as a direct relation to accelerate rock/water interactions and must be used with caution. In general the mineral assemblage produced in short time at high temperature resembles that produced by nature in long time at low temperature, but the fluid compositions in each case are considerably different. The model simulation can closely approximate the evolving fluid composition but it does not account for all the secondary phases actually observed. The relative success in modeling these experiments with the EQ3/6 geochemical modeling code suggests that long term prediction of water chemistry is a potentially achievable goal.

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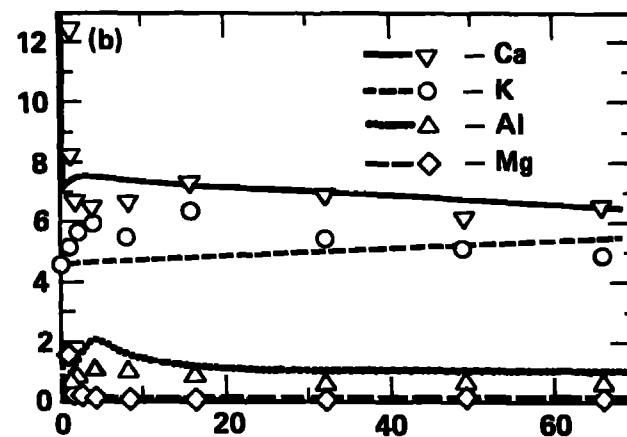
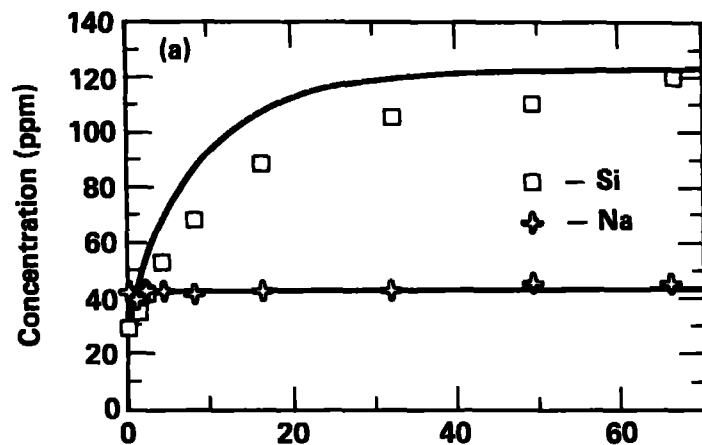


Fig. 1. a) Si and Na concentrations for Topopah Spring tuff reacted with J-13 water at 150°C.
b) Ca, K, Al and Mg concentrations for Topopah Spring tuff reacted with J-13 water at 150°C.
Lines show calculated reaction path model concentrations.

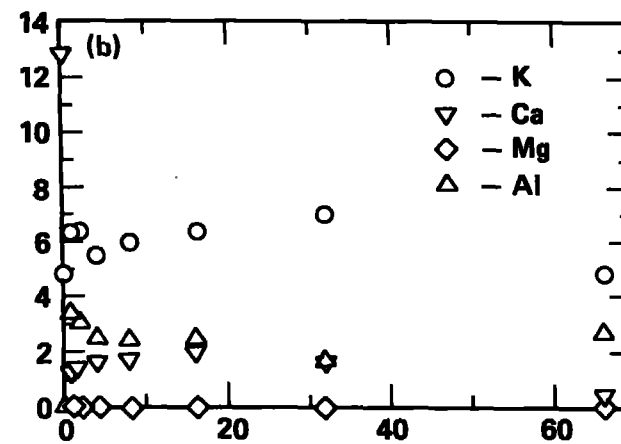
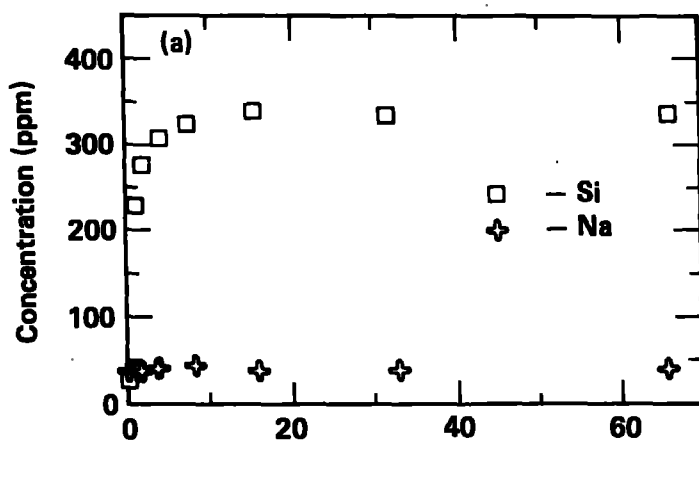


Fig. 2. a) Si and Na concentrations for Topopah Spring tuff reacted with J-13 water at 250°C.
b) Ca, K, Al and Mg concentrations for Topopah Spring tuff reacted with J-13 water at 250°C.



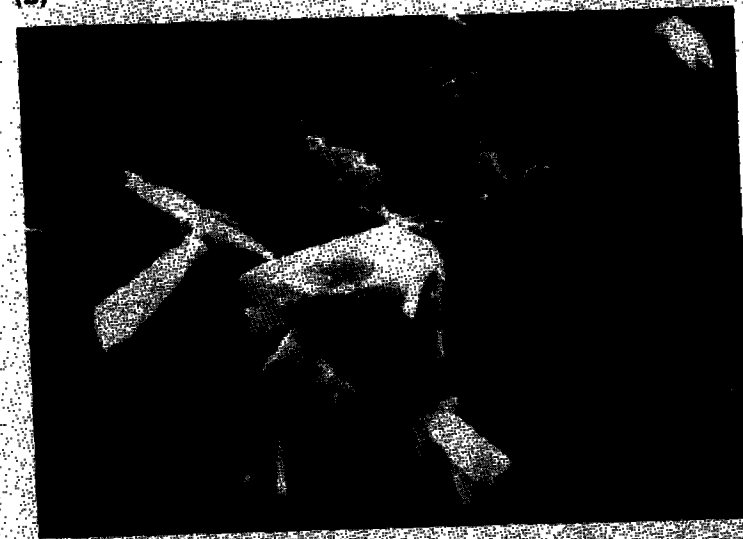
(a) 10 μm



(b) 10 μm



(c) 1 μm



(d) 10 μm

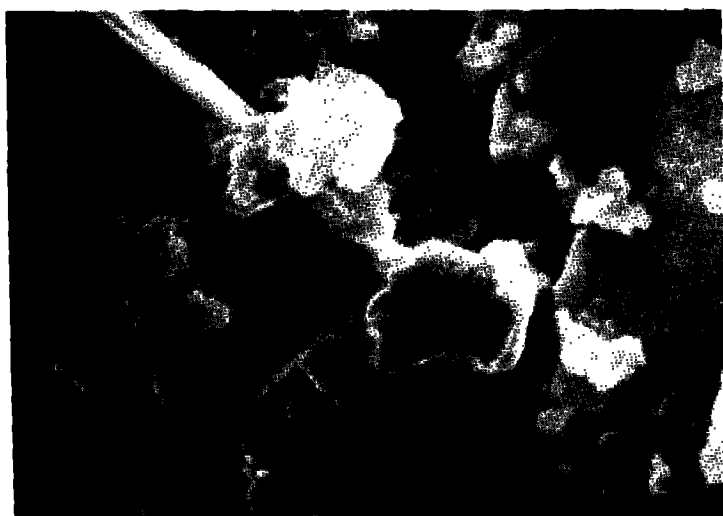
Fig. 3. a) Mg- & Fe-rich clay produced in 150° experiment. b) illite produced in 150°C experiment. c) Gibbsite and illite produced in 150°C experiment. d) Relict (currently dissolving) calcite produced in the 150°C experiment.



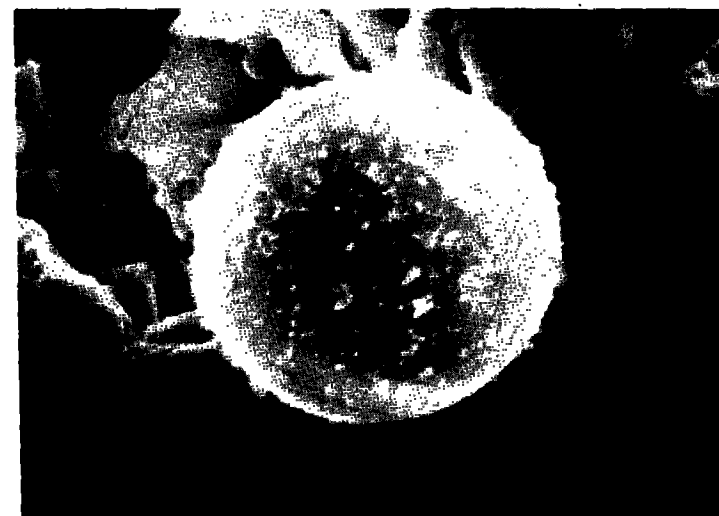
(a) 10 μm



(b) 10 μm



(c) 10 μm



(d) 10 μm

Fig. 4. a) Dachiardite rosette produced in the 250°C experiment. b) Coexisting prismatic dachiardite and mordenite penetrating a dachiardite rosette in the 250°C experiment. c) Ca-rich clay on dachiardite in the 250°C experiment. d) Cristobalite produced in the 250°C experiment.